

Short communication

## Acid loaded porous silicon as a proton exchange membrane for micro-fuel cells

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### Abstract

Silicon-based fuel cells are under active development to supply chip-scale electrical power supply. In this paper, we demonstrate the use of sulfuric acid loaded nanoporous silicon as a proton electrolytic membrane (PEM) material for micro-fuel cell applications. Sulfuric acid loaded nanoporous silicon membranes with thickness of 40–70  $\mu\text{m}$  have proton conductivities (0.0068–0.33 S/cm) comparable to, and in some cases better than, Nafion<sup>®</sup> (0.05 S/cm), which is the most commonly used commercial PEM material. Additionally, the permeability of formic acid at room temperature through nanoporous silicon membranes was found to be similar to that of Nafion<sup>®</sup> membranes, which increases with increasing anodization current density ( $4.3 \times 10^{-8}$  to  $3.9 \times 10^{-7}$  mol/(s cm<sup>2</sup>) for nanoporous silicon as compared to  $1.23 \times 10^{-7}$  mol/(s cm<sup>2</sup>) for Nafion<sup>®</sup> 117). These results represent the discovery of a new class of protonic conductor that can be integrated into standard silicon microfabrication processes.

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### 1. Introduction

In recent papers [1–5], there has been considerable interest in developing silicon-based micro-fuel cells for chip scale power. Most silicon micro-fuel cells have used Nafion<sup>®</sup> as a proton conductor. However, Nafion<sup>®</sup> is not readily integrated with standard microfabrication techniques used in making micro-fuel cells, other microchemical systems, or MEMS based devices [6]. Nafion cannot be easily patterned using photolithography and bonding it to silicon is often problematic in working fuel cell conditions, due to its volumetric changes with changes in hydration level. It would be desirable to develop a solid state protonic conductor that could be readily incorporated into silicon-based devices with performance comparable to that of Nafion<sup>®</sup>.

Innumerable efforts have been made to develop a next generation protonic conducting membrane to replace Nafion<sup>®</sup> for fuel cell applications. Solid-state protonic conductors include materials such as solid acids, polymers, oxide ceramics, and intercalation compounds [7,8]. One common ap-

proach has been to use inorganic–organic hybrid materials, often including Nafion<sup>®</sup> as one of the components. Examples of such composite proton conducting membrane materials reported in the literature include Nafion<sup>®</sup>–silica [9–11], Nafion<sup>®</sup>–borosiloxane [12], and silica–poly(ethylene oxide) [13] composites, among others.

The objective of this work is to demonstrate the potential of nanoporous silicon as a protonic conductor in general, with a specific focus on its potential applications in fuel cells. Porous silicon has been an intensively researched material, primarily due to its unique optical properties. Recently, however, some novel applications have been discovered utilizing other interesting characteristics [14]. Nanoporous silicon is readily formed by anodic etching in hydrofluoric acid. A wide range of porous layer thicknesses, porosities, surface areas and morphologies can be formed depending on the anodization conditions [15]. The nanoscale pore sizes that can be achieved in porous silicon by anodic etching may provide a conduit for proton transport. In an acidic aqueous media, such as in a formic acid fuel cell, the silicon surface is readily oxidized leaving hydroxyl terminated pore surfaces. This hydroxylated surface is known to be acidic [16] and should allow for proton conduction through the nanopores. Furthermore, the nanoscale diameter of the pores may serve

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as a diffusion barrier preventing larger fuel molecules from going through. In principle, the viability of porous silicon as a proton conductor as well as a diffusion barrier to fuel molecules can be further promoted by the functionalization of porous silicon [14,17,18]. A major advantage of porous silicon is its compatibility with conventional Si microfabrication technology, which presents the possibility of fabricating different components of a fuel cell or even a fuel cell and its supported devices in a monolithic fashion. Porous silicon should also be stable at elevated temperatures, unlike many polymeric materials.

In this paper, we have explored porous silicon as an electrolyte in a micro-fuel cell, and provide preliminary evidence that nanoporous is a promising technology for chip scale fuel cell implementations.

## 2. Experimental methods

Nanoporous silicon membranes with a thickness of 40–70  $\mu\text{m}$  were fabricated and tested in this work. Our fabrication scheme is illustrated in Fig. 1. We started with a 100 mm diameter, (1 0 0), p-type, boron doped, 5–20  $\text{m}\Omega\text{ cm}$  resistivity, double-side polished, prime silicon wafer. The wafer was dipped in a buffered oxide etch solution (HF) to remove any native oxide from the exposed silicon surface and a metal layer sputtered on the back side of the wafer to serve as an electrical contact during the anodization process. A chrome adhesion layer topped with gold was used as the metal electrical contact. Dies were patterned on one side of the wafer using a standard photolithography process with four small 1.4 mm diameter circles. Deep reactive ion etching was used to fabricate silicon membranes of desired thickness (40–70  $\mu\text{m}$ ). Anodization was carried out in 25% ethanolic HF solution (49% HF:ethanol = 1:1) under constant current conditions (20–120  $\text{mA}/\text{cm}^2$ ) on each die. The metal/photoresist layer peels off the backside of the sample when the pores penetrate the whole thickness of

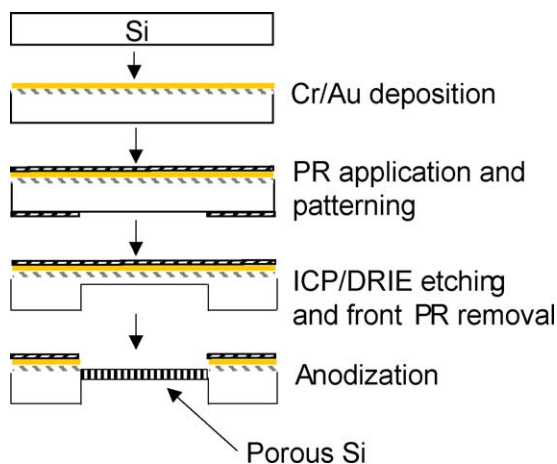


Fig. 1. Fabrication scheme.

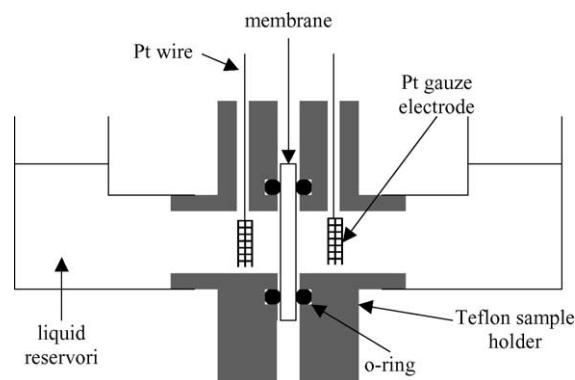


Fig. 2. Apparatus used for impedance spectroscopy and fuel cell testing of membranes.

the membrane. The as-anodized porous silicon surface is hydrogen-terminated. Finally, the remaining photoresist was stripped off the sample and the sample cleaned in a piranha solution ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  (3%), 3:1). In addition to removing residual photoresist, this solution oxidized the exposed silicon surfaces leaving behind a hydroxyl-terminated surface.

Photos of the porous silicon membranes were taken with a Hitachi S4700 FEG (Field Emission Gun) scanning electron microscope (SEM) at the Center for Microanalysis of Materials (CMM) at the University of Illinois in order to physically characterize the resulting membranes. In addition to physical characterization, we examined two key performance metrics for fuel cell membranes, proton conductivity and fuel crossover. Proton conductivity of our porous silicon membranes was determined from impedance spectroscopy measurements. These were done using a VoltaLab PGS100 Potentiostat and platinum gauze electrodes in a glass permeation cell with a Teflon sample holder (shown in Fig. 2). The liquid reservoir on each side of the membrane was filled with 8 M  $\text{H}_2\text{SO}_4$ . A 1 V potential was applied between the two electrodes with frequencies ranging from 10 kHz to 1 Hz and amplitude of 10 mV and resulting impedances measured. Crossover measurements were performed in a similar permeation cell using 5 M formic acid and DI water in liquid reservoirs on either side of the membrane. Changes in pH in the water reservoir were used to determine formic acid flux. Details for the crossover measurement procedures are given elsewhere [19]. Using the same cell as was used for the impedance measurements, a simple fuel cell was constructed. Oxygen was bubbled through a 1 M  $\text{H}_2\text{SO}_4$  solution in the cathode side reservoir of the porous silicon membrane while 5 M aqueous formic acid was in the anode side reservoir. Voltage–current characteristic data was then collected.

## 3. Results and discussion

A typical SEM picture of a porous silicon membrane cross section is shown in Fig. 3. As anodization current density

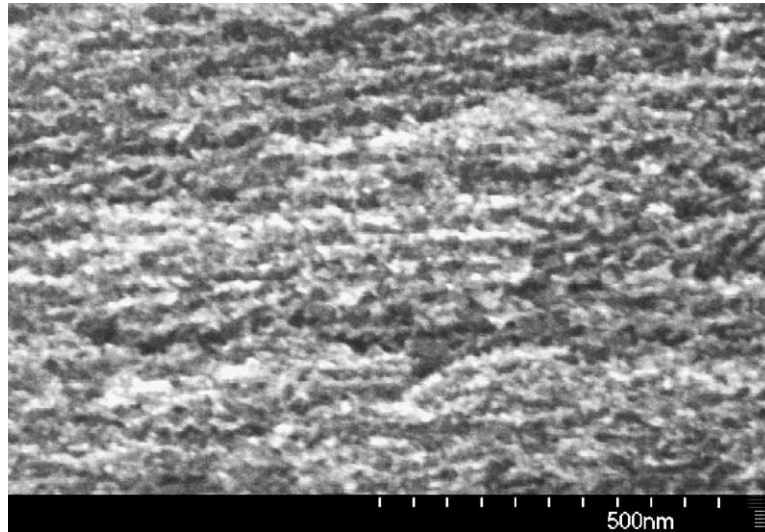


Fig. 3. SEM picture of the cross-section of a porous silicon membrane.

is increased, the pores become larger and straighter, though dendritic in structure and interconnected. At very low anodization current density, the pore structure becomes very random and sponge-like. Typical pore diameters range from  $\sim 20$  nm at anodization current density of  $120 \text{ mA/cm}^2$  to  $\sim 5$  nm at anodization current density of  $20 \text{ mA/cm}^2$ .

Impedance spectra were collected to determine the proton conductivity of the porous silicon and Nafion<sup>®</sup> 117 membranes in sulfuric acid, as well as to gain insight into the conduction mechanism. The impedances of the electrode and solution were subtracted from the data to isolate effects of the membrane. Nyquist  $Z$  plots of the impedance data for the membranes tested are shown in Fig. 4. It is readily apparent that mechanisms of proton conduction in acid

loaded nanoporous silicon are different from that in Nafion<sup>®</sup>. In order to gain some insight into these mechanisms, the impedance data was fit to equivalent circuit models. It should be noted that relating the impedance result to an equivalent circuit is not an exact science, as there is no unique equivalent circuit for a given impedance spectrum. Nonetheless, appealing to accepted models for impedance for double layers, electrokinetic flow resistance, etc. can provide some insight into what is happening within the membranes. The nearly vertical line in the Nyquist  $Z$  plot for Nafion<sup>®</sup> is characteristic of a series RC circuit, which indeed can be used to fit the data. The capacitance in this equivalent circuit model can be explained as the result of the presence of a double layer at the membrane surface. The resistance term results

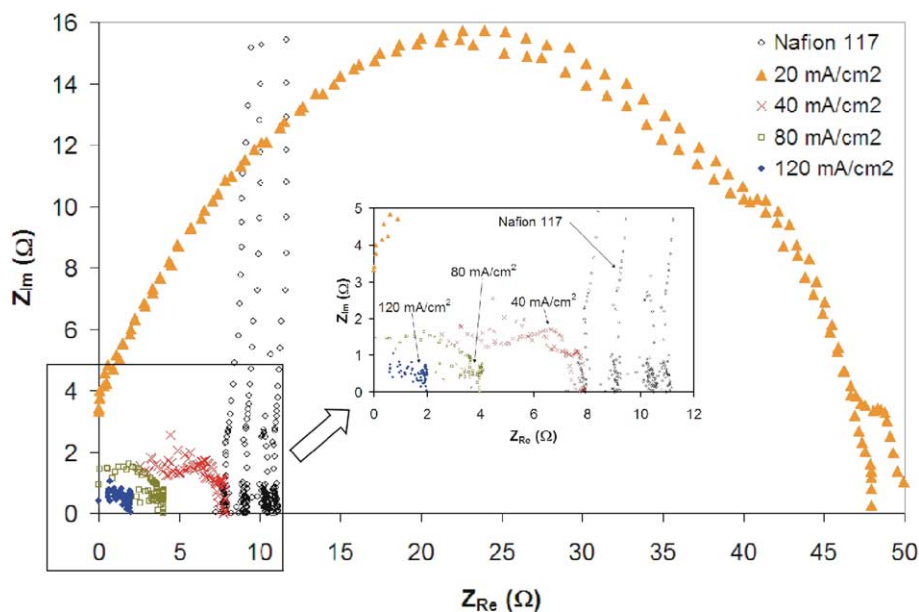
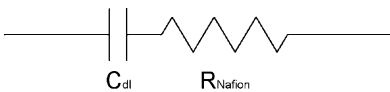
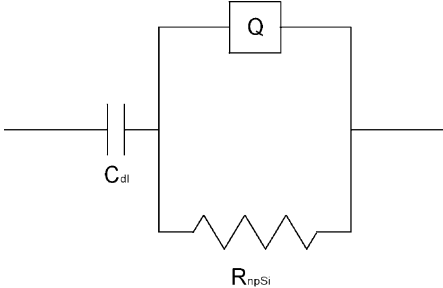


Fig. 4. Nyquist  $Z$  plots of porous silicon and Nafion 117 membranes.

Table 1  
Equivalent circuit fit for Nafion 117 and nanoporous silicon membranes

	$C_{dl}$ (F)	$R_{Nafion}$ ( $\Omega$ )	Equivalent circuit		
Nafion <sup>®</sup> 117	0.07	9.98			
Anodization current density (mA/cm <sup>2</sup> )	$C_{dl}$ (F)	$R_{npSi}$ ( $\Omega$ )	$Q$ (F)	$n$	
Nanoporous silicon					
20	0.33	36.4	$1.7 \times 10^{-4}$	0.82	
40	0.75	5.02	$2.0 \times 10^{-4}$	0.75	
80	0.85	3.47	$1.9 \times 10^{-3}$	0.67	
120	0.09	1.41	$1.5 \times 10^{-3}$	0.75	

from the resistance to proton conduction through the electrolyte membrane.

For nanoporous silicon membranes, it is expected that as pore size increases, membrane conductivity will approach that of the sulfuric acid that fills the pores. As pore size decreases, the resistance to proton transport should increase due to both the increased importance of surface phenomena and the greater physical barrier posed by the smaller pores. Separating these effects is nearly impossible with the current setup. Nonetheless, some insight can be gained by fitting the impedance data to an equivalent circuit.

A semicircular shape in the Nyquist  $Z$  plot is observed for the nanoporous silicon membranes. This shape is characteristic of parallel equivalent circuit elements, indicating two competing mechanisms for the transport of the protons as they pass through the membrane. The equivalent circuit used to model the data is shown in Table 1 and consists of a capacitor in series with a resistor and a non-ideal or leaky capacitor ( $Q$ ) in parallel. The first capacitor is, as with Nafion<sup>®</sup>, due to the presence of a double layer at the membrane surface. The resistor is also analogous to the resistor in the Nafion<sup>®</sup> equivalent circuit and is related to the protonic conductivity of the membrane. This does not however imply that the proton conduction mechanism is the same as in Nafion<sup>®</sup>. In nanoporous silicon, it is likely that this resistance is in large part related to the barrier to proton flow in the nanoscale sulfuric acid loaded pores. The impedance of the non-ideal capacitive element in the equivalent circuit used is equivalent to  $1/Q\omega^n$ , where  $\omega$  is frequency. Thus, when  $n = 1$ ,  $Q$  is an ideal capacitor. The “leaky” capacitor is likely the result of the trapping and release of protons from the nanopore surface via the reaction:  $\equiv \text{Si}-\text{OH}_2^+ \leftrightarrow^K \equiv \text{Si}-\text{OH} + \text{H}^+$ . This reaction is known to occur in an acidic environment [16]. The presence of sulfuric acid in the pores makes it unclear as to the significance of this surface mech-

anism relative to the conduction of protons through the acid present in the pores. Using the resistance values obtained from the equivalent circuit fit, proton conductivities were calculated. This method yields a proton conductivity of 0.04 S/cm for Nafion<sup>®</sup> 117, compared to the reported literature value of 0.05 S/cm [8]. Nanoporous silicon proton conductivities range from 0.0026 S/cm for samples anodized at 20 mA/cm<sup>2</sup> to 0.080 S/cm for membranes anodized at 120 mA/cm<sup>2</sup>. Proton conductivity values are summarized in Fig. 5. It should be noted that the porous silicon membranes are significantly thinner than the Nafion<sup>®</sup> 117 membranes tested. On a per unit area basis, only those nanoporous silicon membranes anodized at 20 mA/cm<sup>2</sup> showed a lower proton conductivity than Nafion.

The crossover flow of 5 M formic acid through the porous silicon membranes at room temperature and open circuit conditions was measured and found to be comparable to that of Nafion<sup>®</sup>. The flux of 5 M formic acid across a Nafion<sup>®</sup> 117 membrane has been previously reported to be  $1.23 \times 10^{-7}$  mol/(cm<sup>2</sup> s) [19]. A significant improvement over Nafion<sup>®</sup> was achieved with nanoporous silicon membranes anodized at 20 mA/cm<sup>2</sup>, which exhibited a crossover flux of  $4.3 \times 10^{-8}$  mol/(cm<sup>2</sup> s). As the anodization current density is increased, crossover flux through the resulting nanoporous silicon membranes also increases, rising to  $3.9 \times 10^{-7}$  mol/(cm<sup>2</sup> s) for membranes anodized at 120 mA/cm<sup>2</sup>. This indicates that formic acid crossover through nanoporous silicon membranes is controlled by pore size. Crossover flux values are illustrated in Fig. 6.

An important test of nanoporous silicon's value as a fuel cell membrane material is its performance in an actual fuel cell. A simple fuel cell was constructed as previously described and the resulting voltage–current characteristic measured. Results are shown in Fig. 7. The open circuit potential (OCP) was found to decrease with increasing anodization

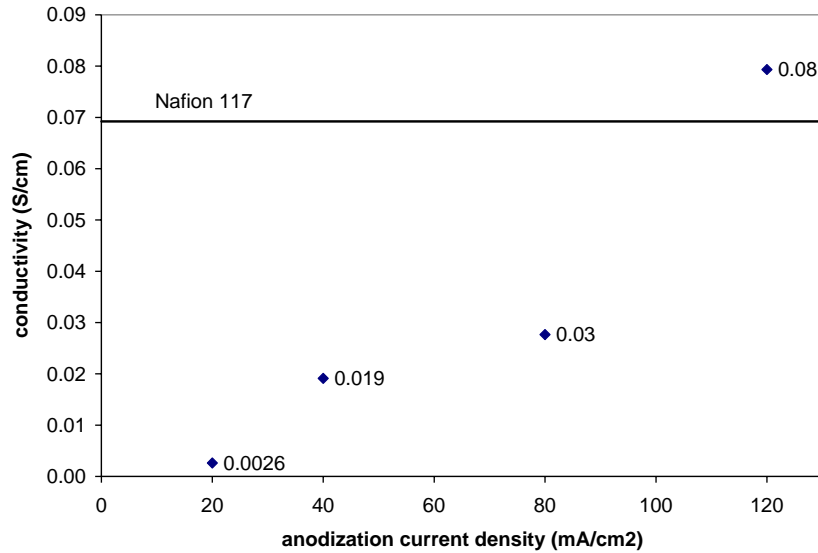


Fig. 5. Proton conductivity of nanoporous silicon membranes as a function of anodization current density.

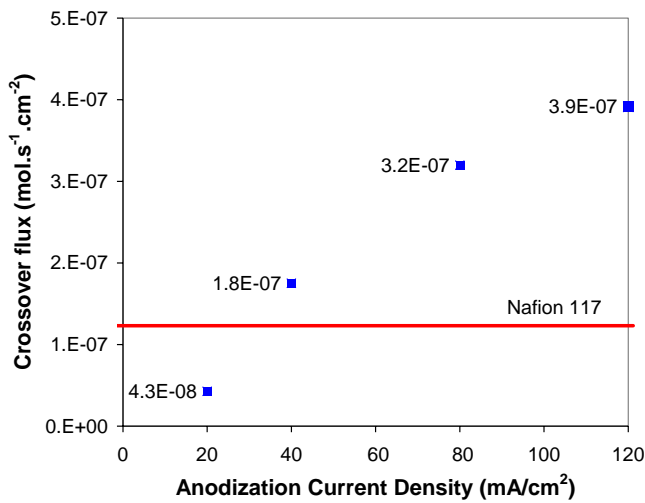


Fig. 6. Crossover of 5M formic acid through nanoporous silicon membranes as a function of anodization current density.

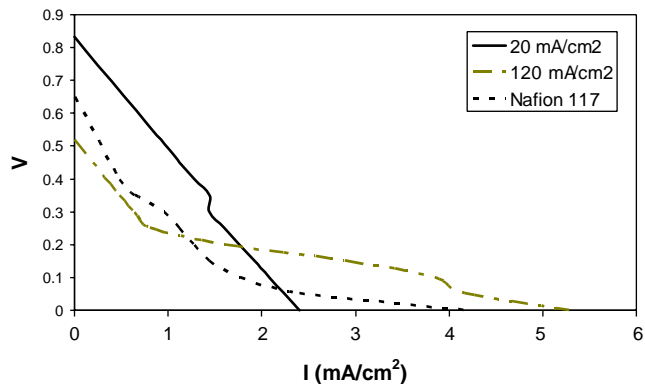


Fig. 7. V-I plot for a nanoporous silicon fuel cell.

current density. This phenomenon is not surprising as the primary effect of fuel crossover in a fuel cell is to reduce the cell OCP. The maximum current was conversely shown to increase with increasing anodization current potential. This increase in current is likely due to the increased proton conductivity observed at higher anodization current densities.

#### 4. Conclusions

Acid loaded nanoporous silicon membranes have been fabricated and demonstrate potential to be used as proton conducting membranes, especially for micro-fuel cell applications. Both proton conductivity and crossover measurements show performance comparable to, and in some cases better than, the current leading commercial electrolytic membrane material, Nafion<sup>®</sup>. The proton conduction mechanism remains unclear but is most likely the result of conduction through the sulfuric acid loaded pores with surface phenomena becoming more important in membranes with smaller pore sizes. Data indicate that formic acid crossover is a function of pore size. The applicability of porous silicon was also demonstrated by its use in a simple fuel cell. Much work remains to be done to understand the proton conduction mechanism as well as to develop the fabrication technology to incorporate electrode and catalyst materials on the membrane surface for a more efficient fuel cell membrane electrode assembly.

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